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EXPERIMENTS WITH ANTIOXIDANTS FOR PREVENTING FLAVOR DETERIORATION IN CANNED ORANGE JUICE[1]

by
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In a previous publication Nolte and von Loesecke (1940) showed that the petroleum ether-soluble material in aged, canned Valencia orange juice had undergone oxidative changes with the creation of hydroxy acids and other decomposition products from the fats and resins, and that the former had become rancid. In view of the evidence presented, it was believed that off-flavors developing in canned Valencia orange juice were due, at least to some extent, to these oxidative changes. The present paper deals with an attempt to prevent these oxidative changes, and hence to prolong the "life" of the canned product, by means of antioxidants. In this connection it may be mentioned that orange juice itself contains natural antioxidants. The most important of these are probably sulfhydryls, ascorbic acid, and sterols. It is quite likely, too, that the sugars, certain amino acids, and proteins have antioxygenic properties, Lea (1939). On the other hand, the juice contains pro-oxidants in the form of traces of copper, iron, and zinc.

The antioxidants used were those believed to be the most promising in the light of recent researches by others. However, such researches have shown that the antioxygenic value of a substance, although high in a particular system, may disappear when this substance is employed in a slightly different system. This seems to be particularly true in systems containing water, as would be the case with orange juice. In the selection of antioxidants their toxicity was considered, but it should be pointed out that some of the antioxidants used in these experiments have not been proved harmless when consumed with foodstuffs. Should such a material be used in foods offered for public consumption, it will be the responsibility of each manufacturer who proposes to use it to establish the harmlessness of the substance before doing so. This is necessary in view of the Federal Food, Drug, and Cosmetic Act.

The kinds and quantities of antioxidants used are indicated (Table 1); these quantities were calculated as being more than sufficient to combine with the oxygen in the juice. In some instances, of course, this could not be calculated. With the exception of "Methyl Glucamine"[2], which was recrystallized three times from water, none of the antioxidants was purified before use. The different chemicals were weighed into No. 4 gelatin capsules which were subsequently placed in the cans. None of the antioxidants in the proportions used caused a foreign taste in the juice. As controls, empty capsules were used. The gelatin was found to be inert.

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2. Supplied by E. I. duPont de Nemours.

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Experimental Procedure

To duplicate the newer commercial practices, the packs were made in a canning plant as part of a regular run. Briefly, the process used consisted of automatically extracting the juice, screening, deaerating, flash pasteurizing at 87.8°C.(190°F.), filling at about 85°C. (185°F.) into both enameled and plain tin cans, and sealing in either nitrogen or air. The oxygen content per "211 x 414" can varied from .03 to .09 cc. The juice had a Brix hydrometer reading of 10.9°, acidity of 1.35 percent as anhydrous citric acid, pH of 3.7, and an oil content of .098 percent by volume. The oil content was unusually high and significantly impaired the quality of the juice. Practically all packs of Florida citrus juices after the January, 1940, freeze showed high oil content. The canned juice was stored at room temperature which varied during the season from -4.5 to 35.5°C. (24 to 96°F.).

Methods of Analysis: Each month the product was subjected to the following tests: sulfhydryl, Taufel's ketone reaction, and peroxide value of the petroleum ether-soluble material of the juice. Since this last test called for the modification of the standard technique, it will be described in some detail. The juice from a "211 x 414" can (which was sufficient for the examination) was fed slowly through a supercentrifuge. It was followed by twice its volume of water. The sludge was removed from the bowl and mixed with sufficient acetone to form a pasty mass. This was transferred to a separatory funnel and extracted five times with 30 cc portions of petroleum ether. The petroleum ether was washed three times with water and the washed ether was filtered into a weighed 250 cc Erlenmeyer flask. Excess ether was removed by distillation and the residue dried at 100°C. (212°F.) for one hour under a blanket of carbon dioxide. The residue thus obtained amounted to from .04 to .1 gram, depending upon the care used in centrifuging and extracting. The weighed residue was dissolved in 10 cc of solvent (six parts glacial acetic acid, four parts chloroform); one drop of 10 percent ammonium molybdate solution was added as catalyst and was followed by approximately .1 gram of solid potassium iodide. The flask was placed in a boiling-water bath for exactly one minute from the time potassium iodide was added. After cooling, the mixture was titrated with .002N sodium thiosulfate, using a microburette. The peroxide value is expressed as the number of cubic centimeters of .002N sodium thiosulfate required per gram of extract.

Discussion of Results

Initially, all of the samples gave a strongly positive sulfhydryl test comparable to that of fresh juice. After a storage period of one month the test was weaker. In two months it became negative, but after reducing the canned product with potassium cyanide, it again became positive. Since sulfhydryls are themselves considered antioxidants -- Josephson and Doan (1939) -- their destruction must result in a loss of at least a part of any natural antioxidant properties the juice might have. None of the added antioxidants in the amounts used either retarded or prevented the destruction of sulfhydryls naturally present in the juice.

The results of Taufel's higher-ketone test coincided quite generally with those of the sulfhydryl test; i.e., they were negative for the first month of storage and positive after the second month. As pointed out in a previous paper by Nolte and von Loesecke (1940), the formation of higher ketones may, in some

instances, be detected by taste and may account for part of the off-flavors in aged, canned orange juice. It was believed that these ketones resulted from the oxidation of higher fatty acids, as well as aldehydes, in the essential oils of the juice. For instance, citral, which may be present in Florida Valencia orange juice -- Nelson and Mottern (1934) -- through the incorporation of peel oil, will yield 2 methyl Δ^2 heptanone and carbon dioxide when oxidized.

Since there was a difference in the oxygen content of the different cans, owing to the commercial technique employed, peroxide values of duplicate or triplicate cans from the same lot varied by as much as 15 percent.

It was found that the antioxidants could be tabulated according to their "protective factor" (PF). This term is defined as the ratio of the length of the induction period (in months) of the juice containing antioxidant to that of juice without antioxidant (Table 2). An antioxidant having a protective factor of 1.0 would be considered inactive.

Since several of the antioxidants used have similar protective factors (Table 2), it was deemed justifiable to combine the results obtained with such antioxidants and plot them as one curve. This is the procedure followed and represented (Fig. 1); it will be observed that the peroxide numbers of the lots vary, and this is quite likely due to the fact that in some cans there was three times as much oxygen originally present as in other cans. Nevertheless, the curves indicate that the induction periods are prolonged from one to five months when using certain antioxidants.

Data for lots containing antioxidants are similar to those presented in Fig. 2; but, to conserve space, they are not plotted. The essential difference between the curves of the control lots (Fig. 2) and those containing antioxidants is the delay in the first induction period of the latter as indicated in Fig. 1. It is evident that the curves of the control lots reveal three induction periods. The first two are distinct, but the induction period after nine months is less apparent, owing to the fact that it occurs before peroxide decomposition of the second induction period has been completed. These three induction periods may be explained by the presence in the orange juice used of three substances -- terpenes, fats, and resins -- which are all capable of forming peroxides. Terpenes and fats form unstable peroxides. In a limited supply of oxygen, after the induction period is passed, the ability of terpenes and fats to form peroxides gradually diminishes as the free oxygen is consumed; decomposition of peroxides already formed then takes place and finally the peroxides disappear. The peroxides of resins, on the other hand, are known to be relatively stable. Since terpenes have been used as antioxidants for fats -- Nakamura (1933) -- it may be assumed that the terpenes present in the orange juice oxidized first, followed by the fats and resins. The order of oxidation, however, is probably of little importance.

While none of the antioxidants used in this study entirely prevented oxidation and flavor deterioration in the experimental packs, the results indicate that the induction period could be prolonged by certain antioxidants. It should be pointed out, however, that no correlation could be found between peroxide value of the petroleum ether extract of the juice and the taste of the juice. Such a correlation was made difficult by the adventitious introduction of peel oil into the experimental packs. Further work is being carried on with the use of other materials having antioxidant properties.

Juice packed in enameled cans possessed a better flavor than that packed in plain tin cans, and this difference was first apparent in three months. It is doubtful, however, whether this difference would be detected by the average consumer. The justification for increased packing cost in enameled cans may, therefore, be questioned.

Nitrogen closure of the containers did not seem to improve the keeping quality of the juice under the conditions of the experiment. In general, however, the peroxide value of the petroleum ether-soluble material from orange juice packed in cans which were nitrogen closed was less than that from juice packed in cans closed in air.

There was no correlation between the vacuum in the cans and the peroxide number of the petroleum ether extract of the juice (Fig. 3).

Summary

Nine antioxidants in different concentrations were added to Florida Valencia orange juice in an attempt to prevent off-flavor development in the canned product. Although some of the antioxidants prolonged the induction period as measured by the peroxide value of the petroleum ether-soluble matter of the canned juice, no correlation could be found between the peroxide value and the taste of the juice. Such correlation was made difficult by the adventitious introduction of peel oil into the experimental packs. As measured by the peroxide number of the petroleum ether-soluble material of canned orange juice, there were three induction periods. This is believed to be due to the successive oxidation of terpenes, fats, and resins in the canned juice, probably in the order named.

None of the antioxidants in the amounts used prevented the destruction of sulfhydryl compounds or the formation of higher ketones in the juice.

Juice packed in enamel cans had a better taste than that packed in plain tin cans, but it is questionable whether the difference could be detected by the average consumer.

There was no correlation between vacuum in the cans and peroxide value of the petroleum ether extract of the canned juice.

Acknowledgement

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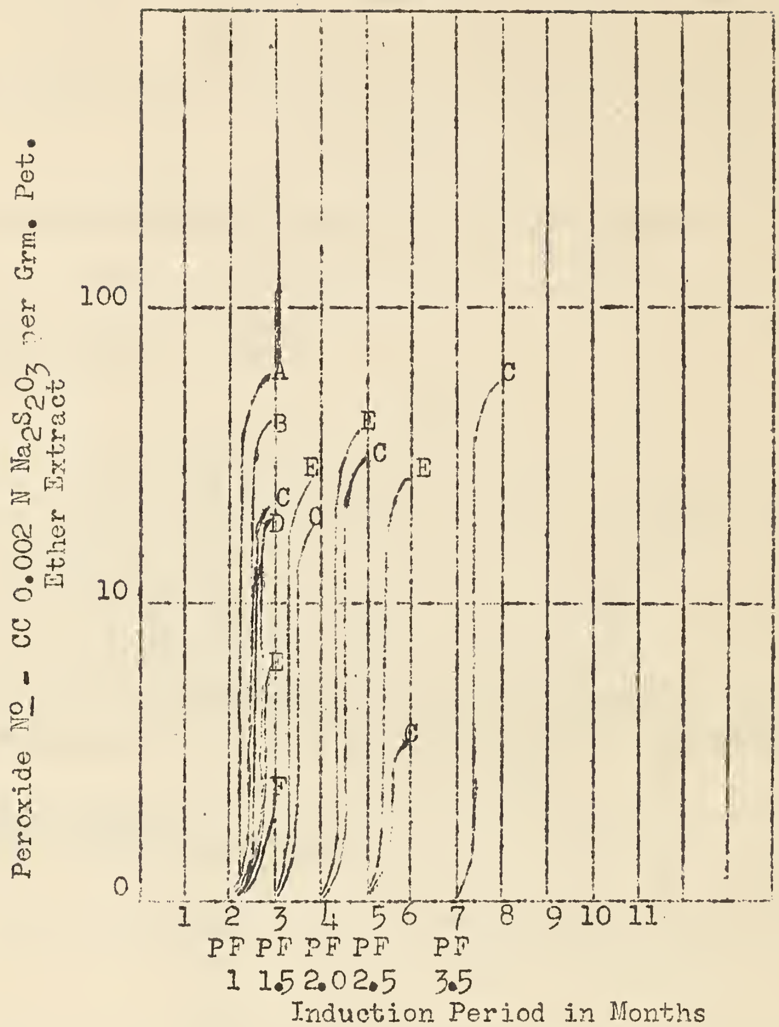
Table 1 - Antioxidants Used Experimentally to Prevent Flavor Deterioration in Canned Valencia Orange Juice

Antioxidant	Quantity used - parts per million parts of canned juice
Asparagine	2,4 and 6
a Naphthol	2,4 and 6
Chloresterol	15,22 and 30
Methyl-p-aminophenol (Elon)	2,4 and 6
d-Isoascorbic acid	30,60 and 100
Hypophosphorous acid	2,4 and 6
Lecithin	2,4 and 6
"Methyl Glucamine"	200 and 500
Resorcinol	2,4 and 6

Table 2 - Protective Factors of Antioxidants as Applied to Canned Florida Valencia Orange Juice

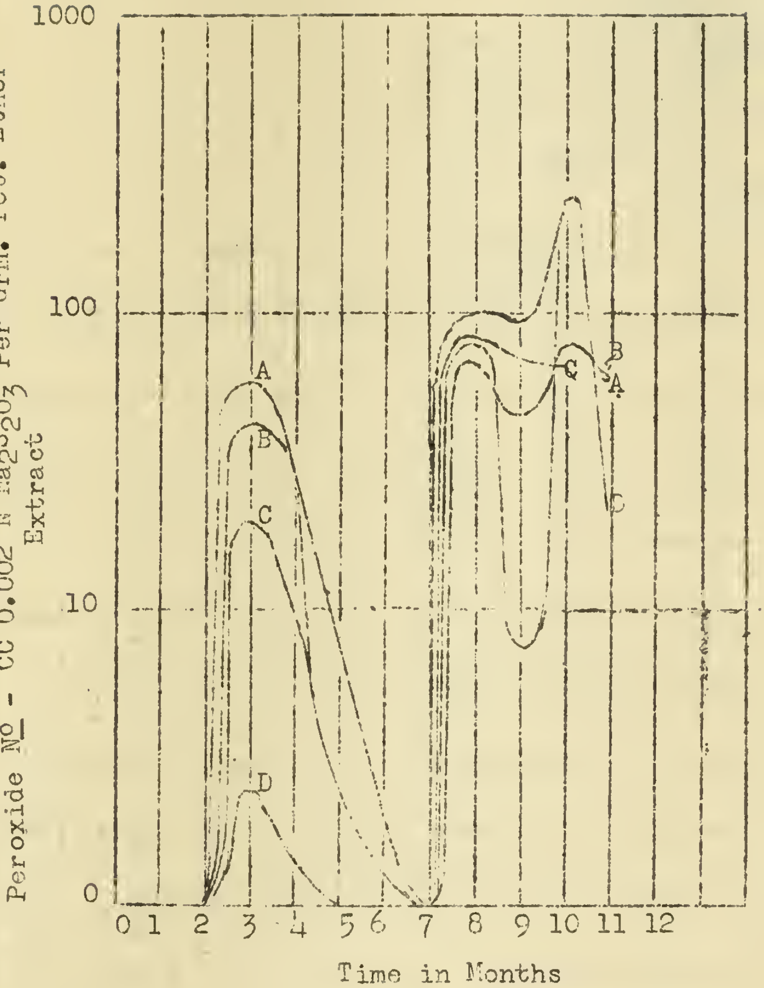
Antioxidant	Protective Factor (PF)	
	In enameled cans	In plain tin cans
d-Isoascorbic acid		
30 p.p.m.	2.0	2.0
60 p.p.m.	2.0	2.0
100 p.p.m.	2.0	2.0
Asparagine		
2 p.p.m.	2.0	2.0
4 p.p.m.	2.0	2.0
6 p.p.m.	2.0	2.5
Lecithin		
2 p.p.m.	1.0	1.0
4 p.p.m.	2.5	2.0
6 p.p.m.	2.5	2.0
Resorcinol		
2 p.p.m.	1.5	1.0
4 p.p.m.	2.0	2.0
6 p.p.m.	2.0	2.0
Hypophosphorous acid		
2 p.p.m.	1.0	1.5
4 p.p.m.	1.0	2.0
6 p.p.m.	2.5	2.0
Chloresterol		
15 p.p.m.	1.0	1.5
22 p.p.m.	1.0	1.5
30 p.p.m.	2.5	1.5
"Methyl Glucamine"		
200 p.p.m.	1.0	1.5
500 p.p.m.	1.0	2.0
a Napthol		
2 p.p.m.	3.5	2.5
4 p.p.m.	3.5	2.5
6 p.p.m.	3.5	2.5
Methyl-aminophenol (Elon)		
2 p.p.m.	1.0	1.5
4 p.p.m.	1.0	2.0
6 p.p.m.	2.0	2.0

Figure 1

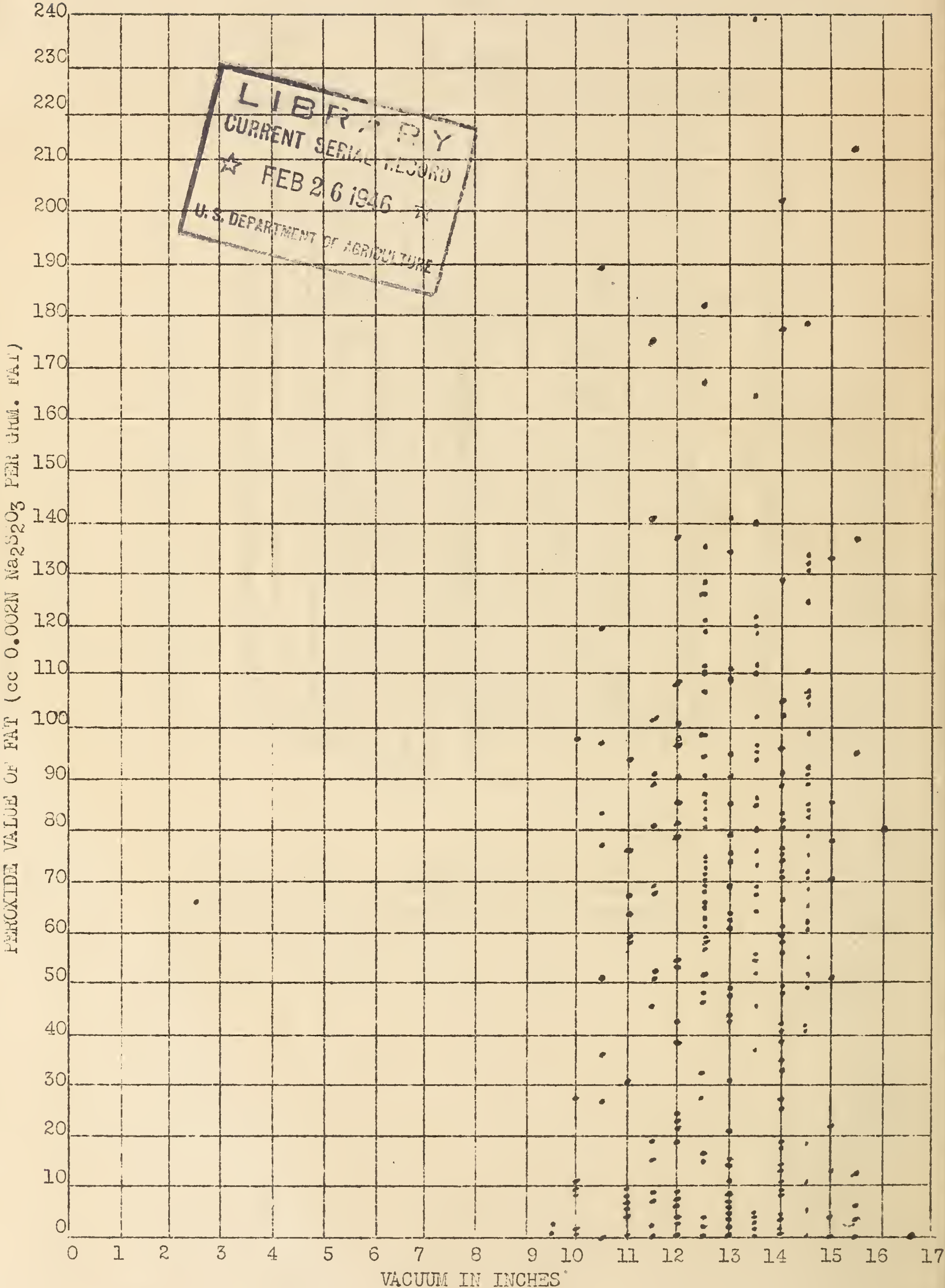


A - Control, tin, closed in air
B - Control, tin, nitrogen closed
C - Enamel with antioxidants, nitrogen closed
D - Control, enamel, closed in air
E - Tin, with antioxidants, nitrogen closed
F - Control, enamel, nitrogen closed

Figure 2



A - Tin, closed in air
B - Tin, nitrogen closure
C - Enamel, closed in air
D - Enamel, nitrogen closure


PEROXIDE VALUE OF FAT (cc 0.002N $Na_2S_2O_3$ PER GRM. FAT)
240
230
220
210
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
50
40
30
20
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0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
VACUUM IN INCHES

FIG. 3